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Depth Profiling of Organic Films with X-ray Photoelectron Spectroscopy Using C_{60}^+ and Ar^+ Co-Sputtering

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By sputtering organic films with 10 kV, 10 nA C_{60}^+ and 0.2 kV, 300 nA Ar^+ ion beams concurrently and analyzing the newly exposed surface with X-ray photoelectron spectroscopy, organic thin-film devices including an organic light-emitting diode and a polymer solar cell with an inverted structure are profiled. The chemical composition and the structure of each layer are preserved and clearly observable. Although C_{60}^+ sputtering is proven to be useful for analyzing organic thin-films, thick organic-devices cannot be profiled without the low-energy Ar^+ beam co-sputtering due to the nonconstant sputtering rate of the C_{60}^+ beam. Various combinations of ion-beam doses are studied in this research. It is found that a high dosage of the Ar^+ beam interferes with the C_{60}^+ ion beam, and the sputtering rate decreases with increasing the total ion current. The results suggest that the low-energy single-atom projectile can disrupt the atom deposition from the cluster ion beams and greatly extend the application of the cluster ion-sputtering. By achievement of a steady sputtering rate while minimizing the damage accumulation, this research paves the way to profiling soft matter and organic electronics.

Because of its high sensitivity to the chemical structure near the outermost layer of a surface and the wealth of useful information it provides, X-ray photoelectron spectroscopy (XPS) is one of the most widely used surface-analysis techniques. Frequently, not only the top atomic or molecular layers are of interest but also the depth distribution of elements in the region close to the surface. Coupled with in situ ion sputtering, the sample can be profiled with high depth resolution.

However, most accepted Ar^+ sputtering techniques fail in analyzing organic thin films and soft matter due to the excessive damage they cause to the surface layer.[1] Hence, information about the newly exposed surface is lost and argon sputtering cannot be used for depth profiling organic materials. Such damage is still observable at low (0.2 kV) beam energy[2] and with other ion species.[3]

Recently, buckminsterfullerene (C_{60}) ion guns were constructed by Ionoptika Ltd.[4,5] and were used to remove the surface layer of specimens. With the use of C_{60}^+ sputtering as the ion source for secondary ion mass spectrometry (SIMS)[6−8] and to remove the surface layer for XPS depth profiling,[2,4,9] a few reports have confirmed that the sputtering yield is increased and the damage to the chemical structure is reduced. In addition, we recently reported that such a sputtering technique can be used to analyze multilayered organic and organic−inorganic composite thin films.[2]

Although the C_{60}^+ erosion is a promising method for depth-profiling organic materials, the sputter rate observed during prolonged sputtering was not constant due to the deposition of amorphous carbon on the surface[2] and ion-induced cross-linking.[10] When equilibrium between sputtering and deposition is reached, the C_{60}^+ ion beam can no longer erode the surface. In this work, a mixture of high-energy C_{60}^+ ions and low-energy Ar^+ ions was established to profile thick organoelectronic devices. With this co-sputtering technique, the chemical states were preserved while a steady sputtering rate was achieved and the probing depth increased dramatically.

EXPERIMENTAL SECTION

XPS spectra were recorded on a PHI 5000 VersaProbe (ULVAC-PHI, Chigasaki, Japan) system using a microfocused (100

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Table 1. Sputtering Times and Observed Chemical Compositions of PEDOT:PSS Thin Films Sputtered with a 10 kV, 10 nA C_{60}^+ Ion Beam and Different Doses of Ar^+ Ions

dose of Ar^+	0	0.2 kV, 75 nA	0.1 kV, 300 nA	0.2 kV, 300 nA	0.1 kV, 600 nA	0.2 kV, 600 nA	0.25 kV, 600 nA	0.3 kV, 600 nA	0.5 kV, 600 nA
sputtering time (min)	5.42	4.24	4.87	3.76	4.87	4.29	4.03	4.49	5.56
composition(C/O/S)	67:24:9	67:24:9	67:24:9	67:24:9	67:24:9	67:24:9	70:21:9	72:20:8	78:14:8

μm, 25 W) Al X-ray beam with a photoelectron takeoff angle of 45°. A dual-beam charge neutralizer (7 V Ar^+ and 30 V electron beam) was used to compensate the charge-up effect. The Ar^+ ion source (FIG-5CE) was operated at various energies using a floating voltage of 500 V. The beam current was adjusted by the strength of the condenser lens. The beam was rastered on an area of 2 mm × 2 mm at an incident angle of 45°. A Wien-filtered C_{60}^+ ion source (IOG C60-10, Ionoptika, Chandler's Ford, U.K.) was operated at 10 nA and 10 kV, with rastering on an area of 2 mm × 2 mm at an incident angle of 70° (70° from the normal to the surface for analysis). The angle between the Ar^+ and C_{60}^+ ion beam was 33°. The ion-beam current was measured with the target current of an Au foil. The base pressure of the main chamber ($<1 \times 10^{-7}$ Pa) was achieved by evacuation using turbomolecular and ion-getter pumps.

The reference specimen for sputter rate measurement was thermally oxidized SiO_2 (28.0, 108, and 229 nm as determined with Mikropack SpecEI-2000-VIS spectroscopic ellipsometer) on Si(100) wafers. Details on the fabrication of the OLED device can be found elsewhere.[11] In short, a hole-transporting layer (HTL) consisting of poly(ethylenedioxythiophene)−poly(styrene sulfonic acid) (PEDOT:PSS), Baytron P VP AI 4083, PEDOT:PSS ~1:4.5) was spin-coated on a 125 nm-thick indium tin oxide (ITO) glass. A light emissive layer (EL) comprising a 4,4′-bis(carbazol-9-yl)biphenyl (CBP) molecular host and doped with Ir-containing dyes was spin-coated on the HTL. Finally, an electron-transporting layer (ETL) consisting of 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBi) was then spin-coated on top of the EL. The fabrication of the inverted polymer solar cell device can be found elsewhere.[12] In short, titanium metal was sputter-coated on ITO glass and was anodic-oxidized to a TiO_2 nanotube arrays with 100 ± 10 nm length and 15 ± 5 nm pore size. The array was annealed in air at 500 °C for 1 h. A thick active layer was spin-coated from a dichlorobenzene solution with P3HT (poly(3-hexylthiophene)) and PCBM ((6,6)-phenyl C60 butyric acid methyl ester) at 1:1 weight ratio. V_2O_5 (10 nm) and Al anode (50 nm) were then thermally evaporated on the active layer.

RESULTS AND DISCUSSION

Although C_{60}^+ sputtering has been proven to be useful for the chemical and structural analysis of soft matter, the depth that the ion beam can sputter through, and therefore the analytical depth, is limited. With the use of reference thermo-oxides on a Si wafer, the sputtering rate is found to decrease significantly with prolonged sputtering (average sputtering rates of 2.5, 2.0, and 1.7 nm/min for 28.0, 108, and 229 nm thick SiO_2, respectively),[2] due to the deposition of carbon on the surface. In addition, chemical changes in the film were observed with high C_{60}^+ ion fluences,[7] so that simply increasing the beam dose to enhance the sputtering depth is disadvantageous. To overcome the limitations of C_{60}^+ sputtering, an Ar^+ ion beam is used here in conjunction with the C_{60}^+ beam to disturb the surface layer and minimize the carbon deposition.

Table 1 lists the sputtering times of a given PEDOT:PSS polymer thin film with different combinations of Ar^+ ion beams. The original data is presented in the Supporting Information. With higher incident energies (above 0.25 kV), the chemical composition of the thin film was altered, indicating that excessive damage occurred during the sputtering. At a given beam current (600 nA), the sputtering rate reached its maximum at 0.25 kV. This result indicates that a low-energy Ar^+ beam enhanced the sputtering rate by disrupting the carbon deposition. However, at higher energy, the Ar^+ beam interfered with the C_{60}^+ beam and the overall sputtering rate decreased. This beam interference could be due to the breakup of C_{60} by Ar^+ ions before it reaches the substrate. Similar behavior was also observed by varying the Ar^+ beam current (75−600 nA) at a fixed beam energy (0.2 kV), i.e., the sputtering rate reaches its maximum at 300 nA. Therefore, an optimized Ar^+ beam dose (0.2 kV, 300 nA) was selected for further research. Under this condition, no excessive chemical damage was observed while the sputtering rate was enhanced.

In a separated experiment, the same PEDOT:PSS polymer thin film was profiled with a 0.2 kV, 300 nA Ar^+ ion beam (Figure S-10, Supporting Information). Even with this low-energy beam, the chemical composition is altered to 83% C, 10% O, and 7% S from 67% C, 24% O, and 9% S. In addition, the time to sputter through the film extended to about 160 min. This extremely long sputter time indicated that the interaction depth of 0.2 kV Ar^+ ion beam is shallow and it altered the structure slowly. With the mixed ion-beams presented here, the shallow damage layer introduced by the low-energy Ar^+ was easily removed by the C_{60}^+ beam and the overall sputtering rate is controlled by the C_{60}^+ beam. Therefore, a reasonable sputtering rate is achieved and the damage to the chemical structure is not observed.

To examine the sputtering rate of a mixed ion beam as a function of the total sputtering time, reference SiO_2/Si specimens (28.0, 108, and 229 nm thick, thermally grown oxide on a (100) Si wafer) were used (Figure 1). A steady sputtering rate (~1.8 nm/min, regardless of the thickness of SiO_2) was observed with co-sputtering using 10 kV, 10 nA C_{60}^+ and 0.2 kV, 300 nA Ar^+ ions, whereas a significant change in sputtering rate was observed without the Ar^+ ion beam.[2]

Figure 2 shows the sputtering depth profile of a multilayered organic LED device using only a C_{60}^+ beam (dotted lines) and a combination of C_{60}^+ and Ar^+ beam (solid lines). Note that the

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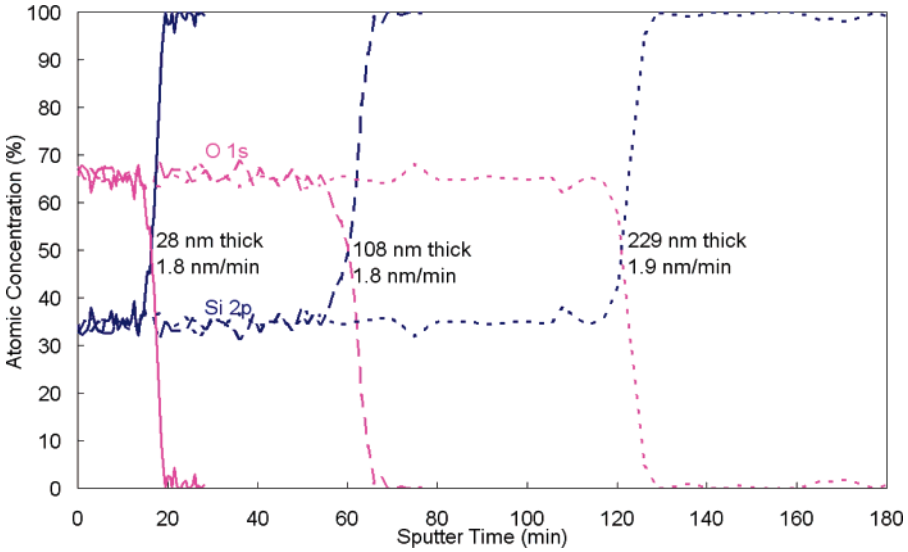

Figure 1. Sputtering depth profile of thermally grown SiO_2 (dotted lines, 229 nm; broken lines, 108 nm; solid lines, 28.0 nm) on Si using 10 kV, 10 nA C_{60}^+ mixed with a 0.2 kV, 300 nA Ar^+ beam.

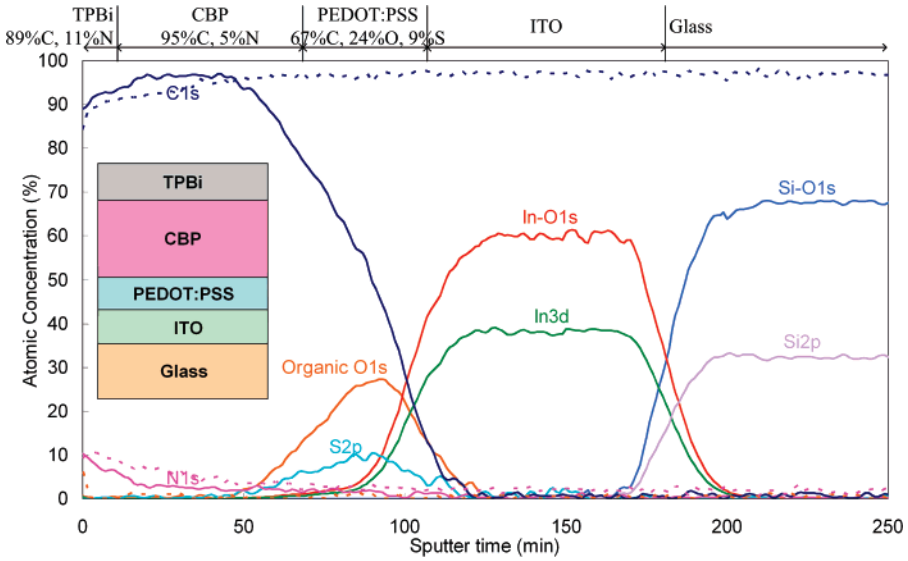

Figure 2. Solid lines: XPS depth profile of organic LED device using 10 kV, 10 nA C_{60}^+ mixed with a 0.2 kV, 300 nA Ar^+ beam. Dotted lines: profiled with 10 kV, 10 nA C_{60}^+ only. The inset shows the schematic of the device structure.

O1s peak was fitted to the contribution of organic oxygen, In_2O_3, and SiO_2 at 532.2, 530.3, and 533.6 eV, respectively. Although excess C was observed, the profile clearly shows the outermost electron-transporting TPBi layer (89% C, 11% N), the light-emitting CBP-host layer (95% C, 5% N) after 20 min, the hole-conducting PEDOT:PSS layer (67% C, 24% O, 9% S) between 70 and 106 min, the ITO electrode (40% In, 60% O), and the SiO_2 substrate.Whereas mixed sputtering successfully sputters through the bottom ITO layer within 200 min, pure C_{60}^+ failed to sputter through the CBP layer even after 300 min.

With the use of mixed-ion sputtering, a polymer based solar cell with inverted structure was profiled (solid lines in Figure 3). The depth profile clearly shows the Al anode and V_2O_5 barrier layer before 80 min, active P3HT:PCBM layer (95% C, 4% S, 1% O) between 80 and 610 min, photoelectrode of P3HT:PCBM infiltred titania nanotube-array between 610 and 860 min, transparent ITO electrode, and the SiO_2 substrate. Note that the C concentration increased (hence, the suppressed concentration of Ti and O) in the organic−inorganic hybrid layer between 610 and 860 min. This change in the chemical composition is due to the P3HT (10∼11 nm, determined with dynamic light scattering in dichlorobenzene) and is comparable with the pore size of the nanotube (15−25 nm), and cross-sectional SEM shows the P3HT did not infiltrate the nanotube completely.[12] On the other hand, PCBM can easily infiltrate the nanotube as it is a small molecule with a diameter of about 1 nm. As a result, there is a composition gradient inside the tube and the concentration of PCBM (hence the C concentration) is higher within the hybrid layer.

Similar to that observed with the OLED device, C_{60}^+ alone failed to sputter through the P3HT:PCBM layer before 1600 min (broken lines in Figure 3). In the early stage of the profiling, the sputtering time for Al decreased from 95 to 65 min with the use of the low-energy Ar^+ beam and the time for sputtering through the V_2O_5 layer decreased from 120 min to 80 min. Because the total ion current increased from 10 nA to about 310 nA, it is arguable that the decrease in sputtering time is the result of the

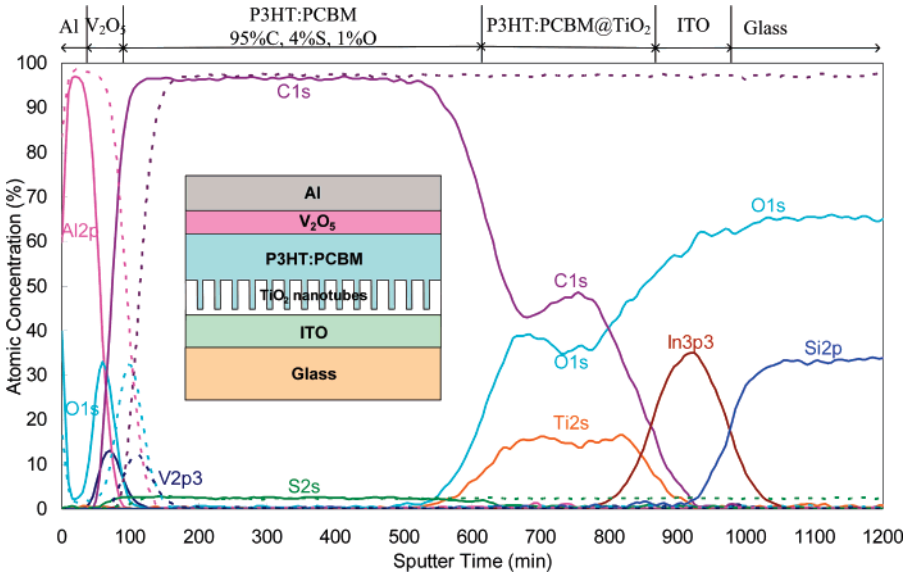

Figure 3. Solid lines: XPS depth profile of inverted polymer solar cell device using 10 kV, 10 nA C_{60}^+ mixed with a 0.2 kV, 300 nA Ar^+ beam. Dotted lines: profiled with 10 kV, 10 nA C_{60}^+ only. The inset shows the schematic of the device structure.

increased current. This possibility is dismissed by the fact that the decrease in the sputtering rate is nonconstant: the ratio of the sputtering rate with and without the use of the Ar^+ beam in the Al layer is 1.46, whereas the rate ratio in V_2O_5 is 1.66 indicating that the sputtering rate decreased with the sputtering time. In addition, if we "scale" the profile linearly based on the assumption of the current effect, the P3HT:PCBM−TiO_2 layer should be observed at about 1100 min. Because it is not observable even after 1600 min, the enhancement in the sputtering rate of mixed-sputtering cannot be simply a contribution from the difference in ion current.

Regardless of the use of the low-energy Ar^+ beam, the carbon composition observed is slightly higher than that expected in both cases. In other words, the observed chemical composition is independent of the use of Ar^+ and the amorphous carbon always deposited. Therefore, the function of the Ar^+ is not to remove the carbon deposition. We tentatively conclude that the function of the Ar^+ beam is to disrupt the deposited carbon film, which cannot be removed by C_{60}^+ sputtering, and the sputtering rate will not decrease with sputtering time significantly.

CONCLUSION

C_{60}^+ ion beams have been proven to be useful for profiling soft matter. However, the effective sputtering rate decreases significantly due to carbon deposition, so that the analysis depth is limited. With the use of a combination of a C_{60}^+ and a low-energy Ar^+ beam, a steady sputtering rate is achieved while chemical and structural damage to the sample surface is minimized. Therefore, multilayered organic devices can be analyzed. To demonstrate the enhanced sputtering ability, an organic LED with a total thickness of ~230 nm and a polymer solar cell with a total thickness of ~485 nm were profiled. The results suggest that the sputtering rate is controlled by the C_{60}^+ beam, and the chemical states are preserved. The function of the Ar^+ beam is to disrupt the carbon deposition so that the sputtering rate of the specimen does not change with time.

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SUPPORTING INFORMATION AVAILABLE

XPS depth profile of PEDOT:PSS using different combination of ion beams. This material is available free of charge via the Internet at http://pubs.acs.org.

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